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Sustainable pathways to chemicals and fuels from lignocellulose via catalytic cleavage and coupling reactions

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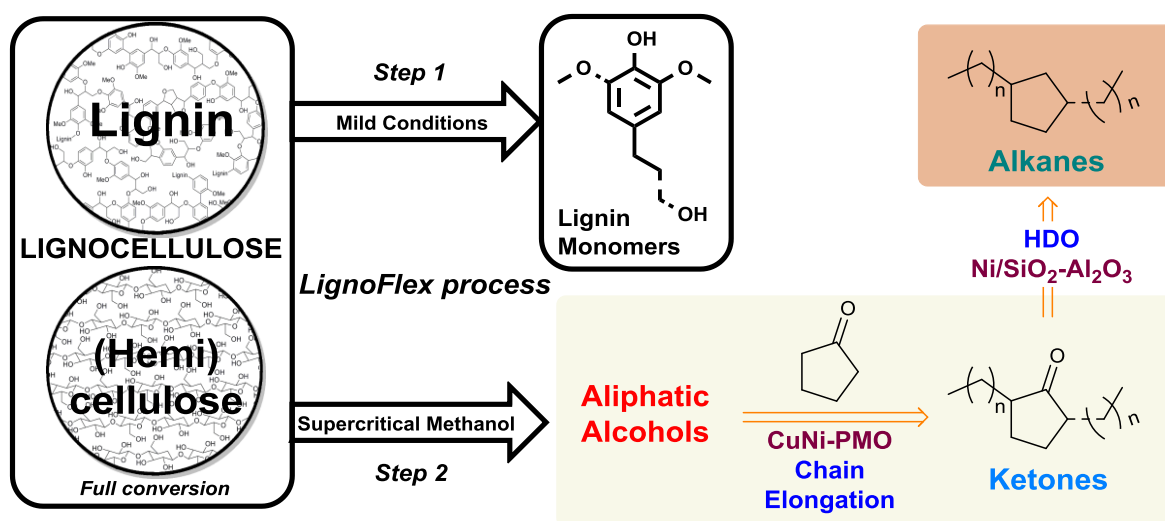
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Chapter 4

Catalytic Conversion of Lignocellulose Derived Alcohols to Fuel-range Alkanes

In Chapter 3, we designed the *LignoFlex* process which transformed lignocellulose to aromatic and aliphatic alcohols (**SMix**). In this chapter I will continue this work and focus on the upgrading of obtained relatively complex mixture of aliphatic alcohols to alkanes. A two steps process, which could efficiently convert the complex aliphatic alcohol mixtures to alkanes via chain elongation and hydrodeoxygenation (HDO) using non-noble-metal catalyst is presented. Cyclopentanone which can be derived from lignocellulosic biomass is selected as the coupling partner for the chain elongation reactions. The obtained ketones are then converted to alkanes by commercial Ni catalyst with a total yield of 54%. The products fell into two main categories: C4–C6 alkanes originating from branched or cyclic uncoupled alcohols, and transportation fuel range, C8–C11, alkanes from the coupling of cyclopentanone with aliphatic alcohols and of lignin-derived propylcyclohexanols.



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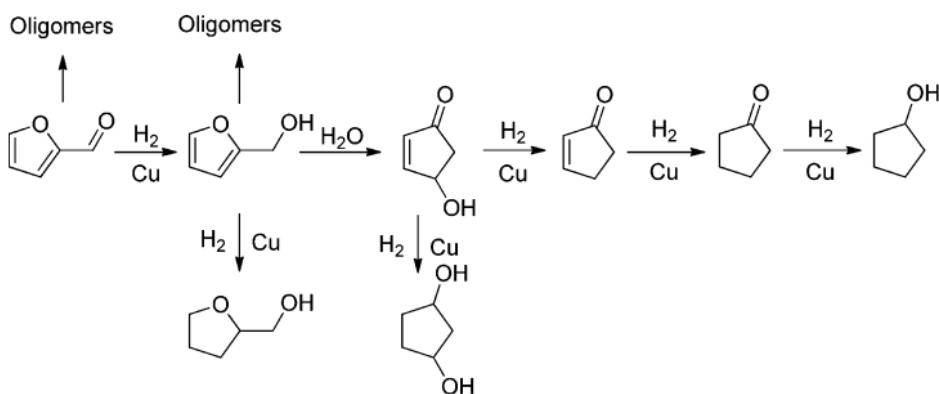
4.1 Introduction

In Chapter 3, I described the newly developed *LignoFlex* process, which delivered a mixture of aliphatic alcohols from the cellulose and hemicellulose fraction of lignocellulose in the second step. This mixture is abbreviated as **SMix**. In principle, this alcohol mixture could be converted to alkanes via hydrodeoxygenation (HDO) reaction, however, the obtained alcohols in *LignoFlex* process contain mainly short chain alcohols (C2-C6), which means the created alkanes via HDO would be too short to be used as fuels.

Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines and normally has high energy density and a low freezing point¹. These requirements are readily met by branched and cyclic hydrocarbons with carbon number between 6 and 16.² However, jet fuel accounts for only about 6% of the refined products of crude oil.³ The aviation industry in all over the world consumes approximately 1.5–1.7 billion barrels (47.25–53.55 billion gallons) of conventional jet fuel annually¹. To fulfill the need of sustainable development, it is required to explore new methods for the production of jet fuels with renewable resource.⁴

Currently, several technologies have been developed for producing renewable jet fuels⁵, which can be categorized by alcohols-to-jet^{6,7}, oil-to-jet⁸, syngas-to-jet⁹ and sugar-to-jet¹⁰ pathways. In recent years, the synthesis of renewable jet fuel by using platform chemicals from lignocellulose has drawn a lot of attentions. For example, furfural has been reported for the production of C8–C15 straight alkanes by the aldol condensation with acetone³, 3-pentanone¹¹ or methyl isobutyl ketone¹², followed by hydrogenation and HDO. Similar strategies have also been reported by using cellulose derived hydroxymethylfurfural (HMF)¹³ and 2-methylfuran¹⁴.

Recently, it was found that cyclopentanone can be also used as a potential building block for the synthesis of diesel and jet-fuel range cycloalkanes^{15,14,16–19}. For example, from the hydroxyalkylation/alkylation (HAA) of cyclopentanone with 2-methylfuran followed by HDO, a mixture of C9–C15 branched alkanes and cycloalkanes can be produced.¹⁴ It was also reported that high-density (0.82 g mL⁻¹) jet-fuel range cycloalkanes can be synthesized in high overall yields (~80%) by the aldol condensation of cyclopentanone with butanal followed by a HDO reaction.¹⁷



Scheme 4.1 Reaction Pathway in Furfural Hydrogenation to cyclopentanone with CuZnAl catalysts proposed by Zhang et al.²⁰

Cyclopentanone has a cyclic structure and can be obtained by catalytic conversion of furfural^{20,21} (Scheme 4.1) - which is exclusively produced from renewable agricultural waste sources such as food crop residues.^{22–27} Due to the increased demand, the furfural market volume is projected to be ~0.5 Mt annually with an estimated annual growth rate of 4.3%, while its price has been in the range of \$900–1000 per ton.²⁸ Nowadays bioethanol (producer price) is around 0.6\$ per liter (density: 789kg/m³), which means 1267 \$ per ton in contrast with the price of furfural between 900–1000\$ per ton.²⁹ Furfural can be quantitatively transformed to cyclopentanone using heterogeneous catalysts, through scalable procedures^{25,30} with excellent 82% atom economy, whereby all carbon atoms are incorporated into the product and water is the only byproduct. Therefore, cyclopentanone is a very appealing coupling partner.

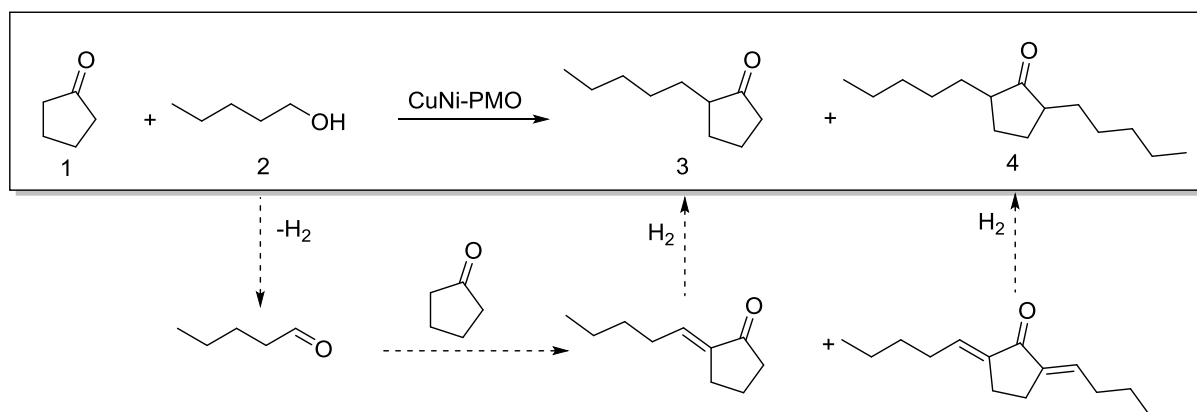
Based on these literature studies, I envisioned that the products from step 2 of the *LignoFlex* process, which comprise mainly aliphatic alcohols, can also undergo coupling reaction with cyclopentanone. In this chapter, I will present the development of a new strategy for production of jet fuel range alkanes with alcohols and cyclopentanone. In this strategy, alcohols are first converted to long chain ketones via a dehydrogenation and aldol-condensation reaction sequence, following HDO reaction that could convert all formed ketones to alkanes. Notably, for both steps non-noble metal catalysts were used. It is important to mention that the **SMix** mixtures in hand are relatively complex, but consist mainly of aliphatic alcohols and also many isomers. Upon coupling and subsequent HDO, by removing the oxygen content, the product mixture converges into less complex mixtures with high selectivity and yields.

4.2 Results and discussion

4.2.1 Coupling of cyclopentanone using alcohol model compounds

Following on the precedence that described the coupling of cyclopentanone with butanal,¹⁷ I envisioned that in similar fashion, 1-pentanol could also be coupled after an appropriate

dehydrogenation step. I consider 1-pentanol as a model compound representative for the more complex reaction mixture of aliphatic alcohols and employed 1-pentanol to establish suitable reaction conditions for the desired carbon-carbon bond formation. The reaction should take place following the sequence of steps shown in Scheme 4.2: a.) 1-pentanol is first dehydrogenated to 1-pentanal. b.) It subsequently undergoes aldol condensation with cyclopentanone facilitated by the basic sites of the PMO catalyst and c.) the product of the aldol condensation would then undergo hydrogenation to the corresponding saturated ketone via the hydrogen generated in the first dehydrogenation step.



Scheme 4.2 Proposed reaction pathways for coupling of cyclopentanone and 1-pentanol.

Table 4.1 Coupling of 1-pentanol with cyclopentanone at different reaction conditions.

Entry	Catalyst	Cyclopentanone (mmol)	1-Pentanol (mmol)	T (°C)	Conversion of 1-Pentanol (%)	GC selectivity of 4 (%) ^a
1	Mg/Al-PMO	1.1	0.46	150	89	12.4
2	Mg/Al-PMO	1.1	0.46	180	84	9.8
3	Mg/Al-PMO	1.1	0.46	200	76	12.9
4	Mg/Al-PMO	1.1	0.92	180	44	10.2
5	Mg/Al-PMO	0.55	0.92	180	40	25.5
6	CuNi-PMO	0.55	0.92	180	63	61.9

Reaction conditions: heptane 3 mL, catalyst 0.05 g, dodecane 10 μ L, 18h.

a. selectivity of 2-pentylcyclopentanone based on GC area percentage.

I first selected Mg/Al-PMO, which is known to be solid base catalyst for a variety of aldol condensation reactions and were also used in similar transformations involving acetone and furfural as well as primary alcohols and furfural.^{11,31–35} The results of this screening are shown in entries 1-5, Table 4.1. While a good conversion of 1-pentanol was seen, relatively low 2-pentylcyclopentanone selectivity was obtained due to the self-coupling of cyclopentanone, which produced [1,1'-bi(cyclopentan)]-2-one as the main product. Changing of temperature didn't influence the conversion and selectivity, and increasing the relative amount of 1-pentanol did not sufficiently increase product selectivity. I have then selected a porous metal oxide containing both Cu and Ni dopants that has demonstrated more affinity for alcohol dehydrogenation and was developed in our laboratory for the highly selective

Guerbet reaction of ethanol to 1-butanol.³⁶ Gratifyingly, this catalyst provided much better results in the coupling of 1-pentanol with cyclopentanone at 180 °C (Table 4.1, Entry 6).

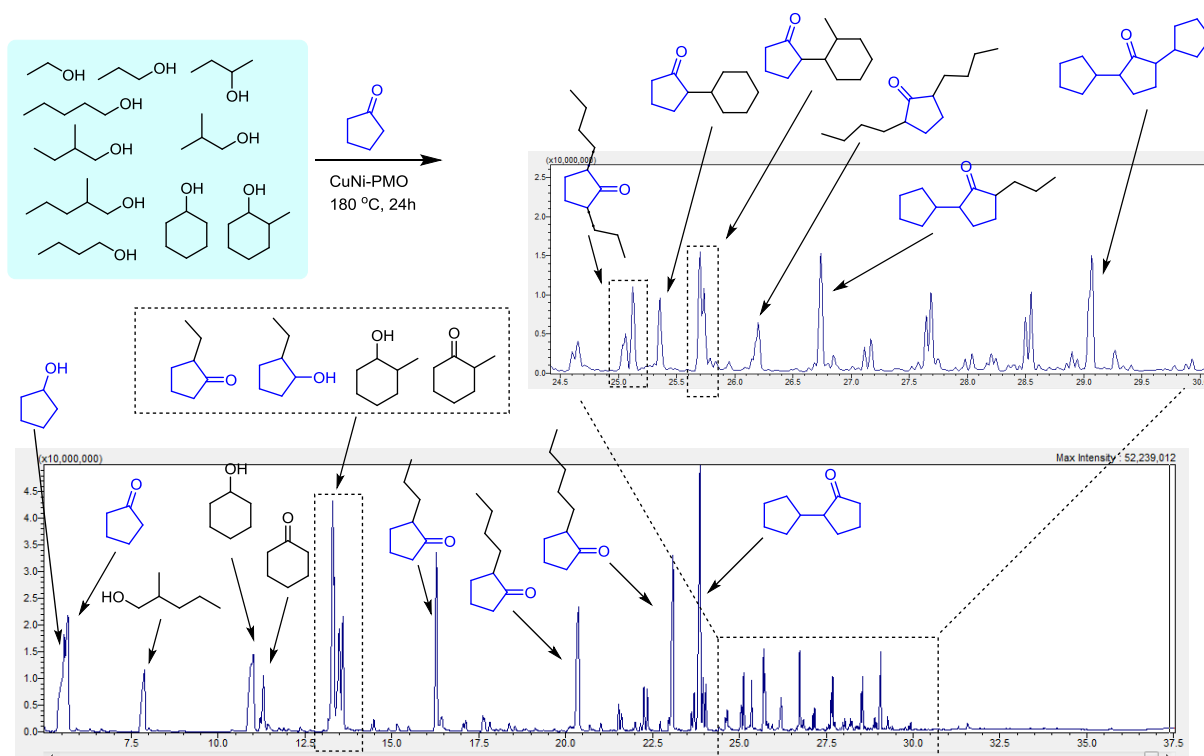


Figure 4.1 GC-MS chromatogram of the products obtained after coupling of cyclopentanone with the model alcohol mixture. Reaction conditions: alcohol mixtures 0.1 mL (1.07 mmol), cyclopentanone 0.05 mL (0.55 mmol), CuNi-PMO 0.1 g, heptane 3 mL, 180 °C, 24 h.

After establishing ideal reaction conditions for the coupling of cyclopentanone with 1-pentanol, a model mixture of alcohols that are representative for the composition of **SMix** (obtained from *LignoFlex*) was prepared and tested. The mixture contained 10 different aliphatic alcohols including ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 2-methyl-1-pentanol, cyclohexanol and 2-methylcyclohexanol which were mixed with equal volume of 1 mL. To the best of our knowledge, coupling of mixtures of such high complexity has not been previously accomplished. Gratifyingly, under the previously established reaction conditions, efficient coupling was observed, although not all components reacted equally well (Figure 4.1). The peaks were identified by analyzing molecular and fragment ions. The long chain primary alcohols efficiently coupled with cyclopentanone. The linear primary alcohols coupled preferentially 1:1 with cyclopentanone, resulting in C7-C10 ketones, but coupling of 2 equivalents of these primary alcohols with 1 equivalent of cyclopentanone was also seen, resulting in C11-C15 ketones. Interestingly, a reaction between cyclopentanone as well as methyl-cyclohexanol with cyclohexanol was also observed. Self-coupling products of cyclopentanone were also seen. Branched 2-methyl-1-pentanol as well as the cyclic cyclohexanol and methyl-cyclohexanol were partially dehydrogenated, but did not undergo efficient coupling reaction due to steric hindrance.

Determining that efficient coupling occurred with most linear alcohols and establishing good analytical practices, I have moved towards optimization reactions using the **SMix** directly as described below.

4.2.2 Coupling of cyclopentanone with alcohol mixtures from *LignoFlex* process

I have performed a solvent exchange from methanol to heptane prior to coupling of the alcohols obtained from pine lignocellulose with cyclopentanone. This was necessary because methanol solvent hampered efficient coupling reaction. Methanol was removed by distillation in a special distillation apparatus equipped with an oil/water separator filter funnel, at 105 °C. After distillation, a light yellow heptane solution containing most of the alcohol products was obtained. As can be seen from the GC-FID traces in Figure 4.2, most of the aliphatic alcohols were successfully transferred into heptane, while there was also a small amount of heptane insolubles (brown oily material). Based on the analysis of GC-MS (Figure 4.3), the heptane insoluble oil contains mainly alcohols and small amount of ethers, esters and phenolics, which originate from residual lignin in the lignocellulose.

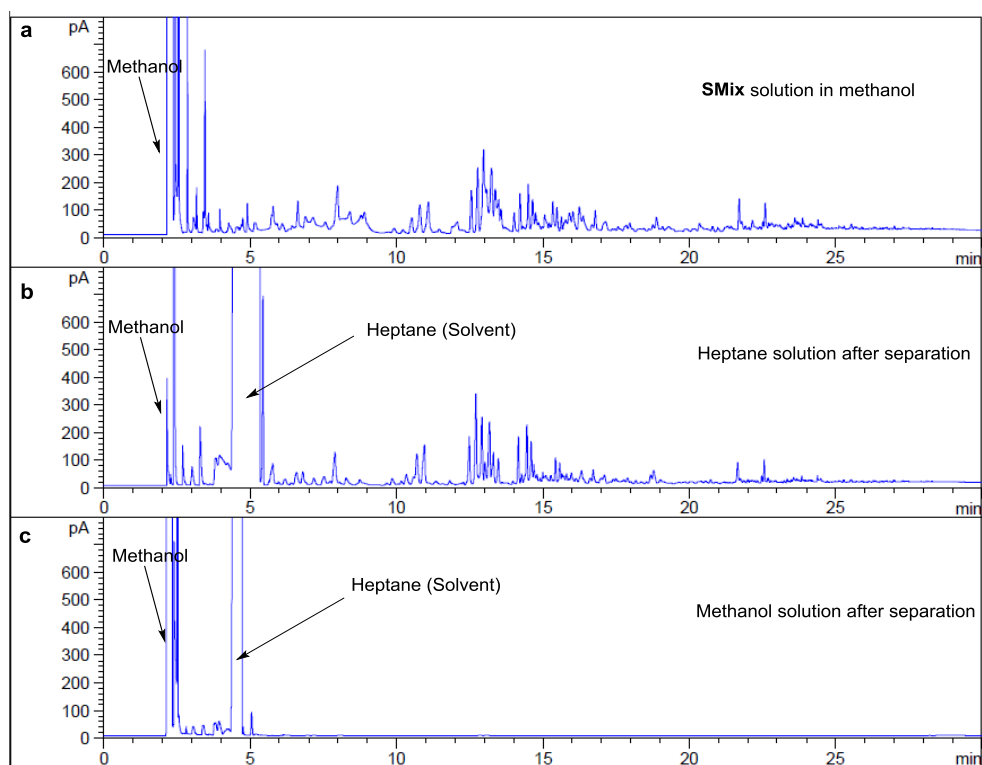


Figure 4.2 GC-FID chromatograms of the solvent exchange procedure. a: **SMix** solution in methanol; b: Heptane solution after distillation of methanol showing that most aliphatic alcohols remained in heptane; c: Methanol solution showing negligible amount of alcohols.

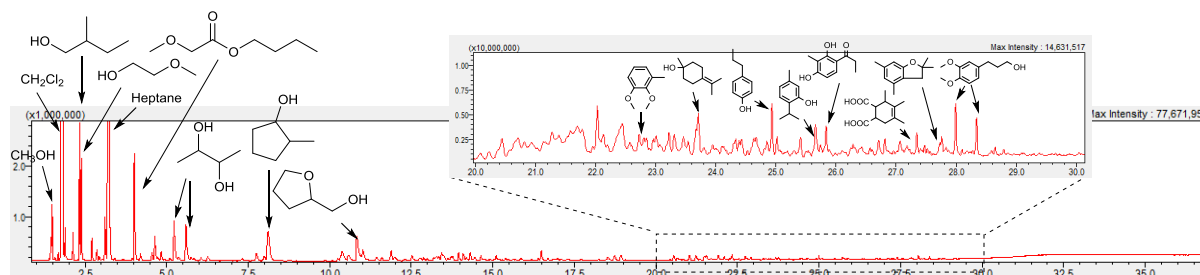


Figure 4.3 GC-MS chromatogram of the heptane insoluble oil (~30 mg, solubilized in DCM).

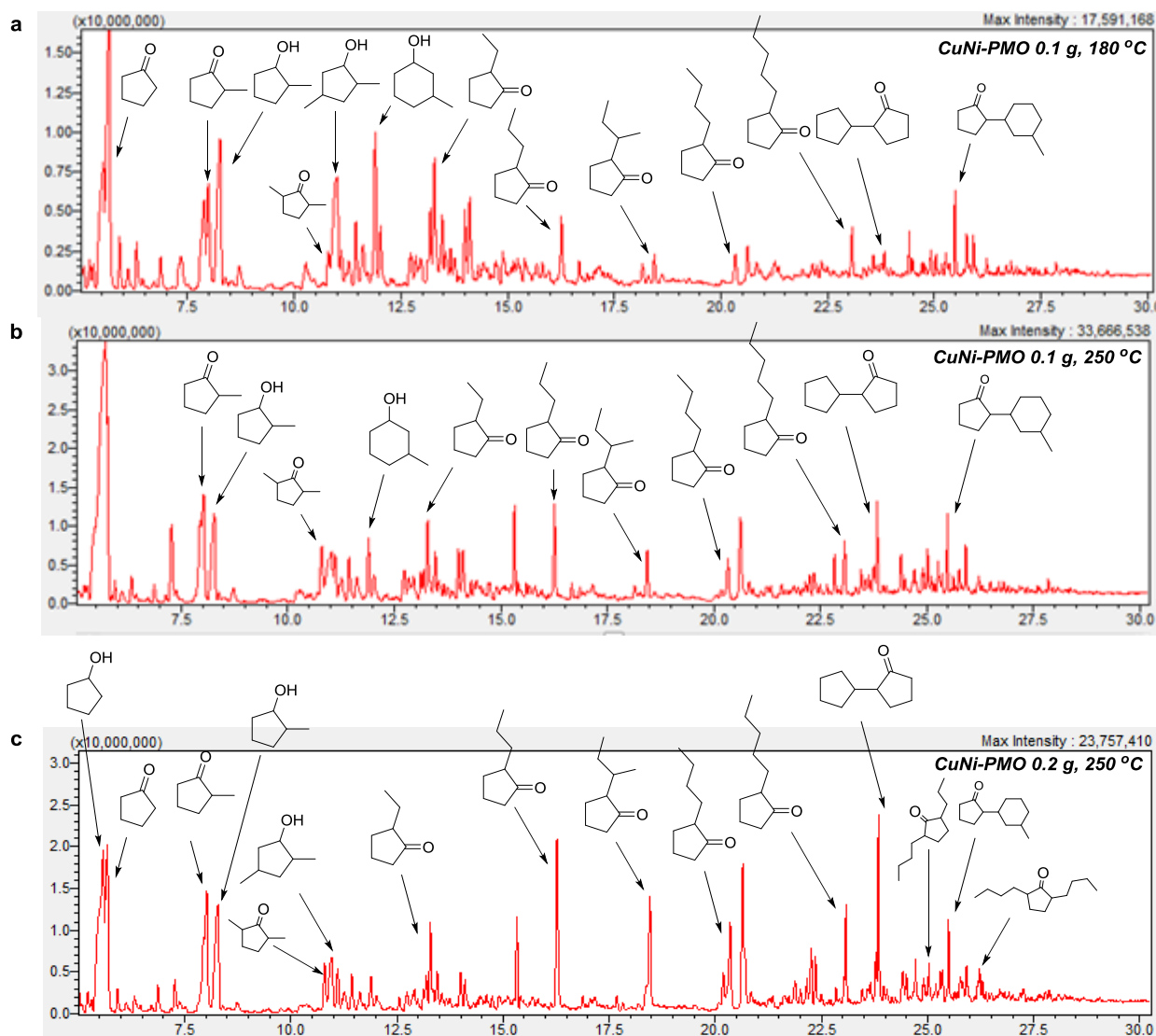


Figure 4.4 GC-MS chromatograms of the products obtained upon coupling of cyclopentanone with the alcohols from pine solid residue **SMix**. Reaction conditions: cyclopentanone 0.05 mL (0.55 mmol), heptane 3 mL, 24 h.

Coupling of **SMix** from pine lignocellulose was first performed under previously established reaction conditions at 180 °C, however only a few longer chain ketones were observed (Figure 4.4a). This could be attributed to the complex composition of **SMix** and presence of esters and ethers. In order to deliver sufficient yields of longer chain ketones, I increased the

temperature to 250 °C and subsequently increased the catalyst loading. This delivered very good selectivity of the desired long chain ketones (Figure 4.4c). The majority of signals (more than 90%), especially the main products were identified by GC-MS measurements and described in Table 4.2. Due to the complexity of the mixtures obtained, the quantification of the products was performed in great detail after the hydrodeoxygenation reaction described in below in Chapter 4.2.3.

Table 4.2 Complete overview of GC-MS signals, identification of products after coupling of cyclopentanone with **SMix**.

Peak	Time (minutes)	Area	Area %	Identification	Quality match %
1	5.581	70306867	7.91	Cyclopentanol	86
2	5.681	97538775	11.01	Cyclopentanone	84
3	7.942	26779749	3.01	Cyclopentanone, 3-methyl-	98
4	8.025	49907679	5.62	Cyclopentanone, 2-methyl-	98
5	8.282	74136530	8.34	Cyclopentanol, 2-methyl-	95
6	10.797	20024487	2.25	Cyclopentanone, 2,5-dimethyl-	91
7	10.964	34980102	3.94	2,4-Dimethylcyclopentanol	82
8	11.106	15089374	1.7	Cyclopentanone, 2,5-dimethyl-	88
9	11.441	11465207	1.29	Cyclohexanone, 4-methyl-	75
10	11.888	10365255	1.17	Cyclohexanol, 3-methyl-	72
11	13.286	27773523	3.13	Cyclopentanone, 2-ethyl-	87
12	13.451	14256193	1.6	Cyclohexanol, 2-methyl-	87
13	13.995	11291908	1.27	3-Methyl-2-butenic acid, 2-tetrahydrofurylmethyl ester	76
14	15.326	21001087	2.36	Not identified	-
15	16.271	61152266	6.88	2-Propylcyclopentanone	86
16	18.46	35753812	4.02	Cyclopentanone, 2-(1-methylpropyl)-	86
17	20.189	11336553	1.28	not identified	-
18	20.348	39105599	4.4	2-Butylcyclopentanone	85
19	20.649	59548455	6.7	4,4,6-Trimethyl-cyclohex-2-en-1-ol	76
20	20.7	9570838	1.08	1,2-Cycloheptanediol	80
21	22.259	18008657	2.03	not identified	-
22	22.362	12118367	1.36	not identified	-
23	23.078	23534159	2.65	2-Pentylcyclopentanone	87
24	23.78	11981747	1.35	2-Naphthalenol, decahydro-	78
25	23.845	46826910	5.27	[1,1'-Bicyclopentyl]-2-one	92
26	24.414	10063740	1.13	Benzene, 4-ethyl-1,2-dimethoxy-	77
27	24.498	4006788	0.45	not identified	-
28	24.714	10006871	1.13	2-Hexylcyclopentanone	74
29	24.898	6703457	0.75	2-butyl-5-propylcyclopentanone	a
30	25.033	7140634	0.8	Cyclopentanone, 2-(5-oxohexyl)-	69
31	25.489	19758699	2.22	1,2-Dimethoxy-4-n-propylbenzene	a
32	25.914	7507635	0.85	2-(3-methylcyclohexyl)cyclopentanone	a
33	26.223	9368872	1.05	2,5-dibutylcyclopentanone	a

a. peaks were identified based on molecular weight and comparison with the results from model compound study.

4.2.3 HDO of the ketones obtained from the coupling of SMix with cyclopentanone to alkanes

Based on literature studies that employed Ni/SiO_2 ¹⁷ and $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ ¹⁴ catalyst for the HDO of ketones to alkanes, I have selected the commercially available $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ to establish the method for efficient HDO of the mixtures of ketones obtained upon coupling of lignocellulose derived aliphatic alcohols contained in **SMix**. First, 4-propylcyclohexanone was selected as model compound to test the activity and stability of this catalyst for the HDO reaction. As shown in Figure 4.5, this catalyst showed extremely high robustness. Next, we have used the mixtures of ketones obtained upon the coupling of the selected, standard mixture of alcohols with cyclopentanone. Full HDO was seen and clear mixtures of alkanes in heptane were obtained (Figure 4.6). Next, I used these established reaction conditions to perform HDO on the ketones obtained after coupling with **SMix**. Also here, full conversion of the ketones was seen. It is important to note, that the shorter aliphatic alcohols and ketones that did not undergo coupling reaction also underwent efficient HDO to alkanes (Figure 4.7), albeit with shorter chain length. The heptane insoluble oil which contains mainly alcohols and small amount of ethers, esters and phenolics also underwent efficient HDO to alkanes (Figure 4.8).

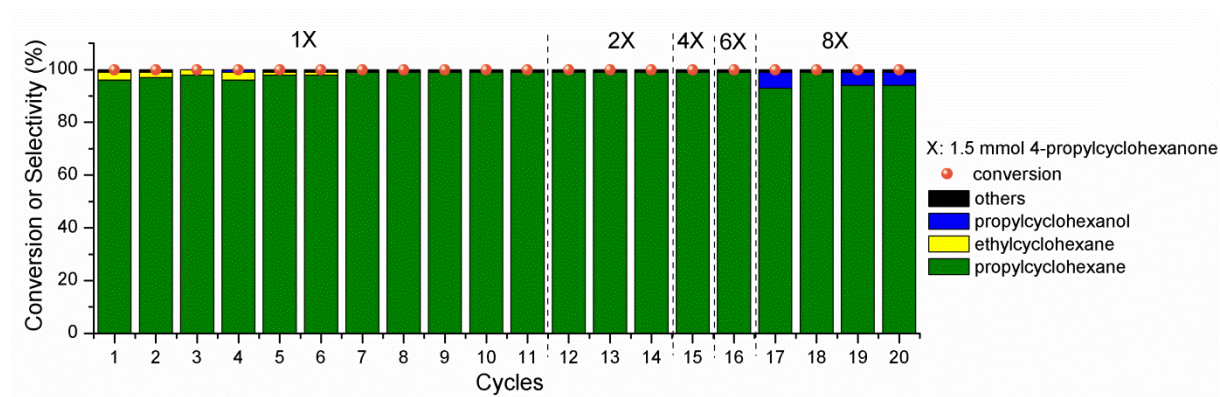


Figure 4.5 Recycling test of catalytic HDO by $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ using 4-propylcyclohexanone as model compound. Reaction conditions: 4-propylcyclohexanone 1.5 mmol, heptane 10 mL, $\text{Ni/Al}_2\text{O}_3\text{-SiO}_2$ 0.2 g, 250 °C, 6 h, H_2 40 bar. Note: the substrate amount was increased after 11 cycles.

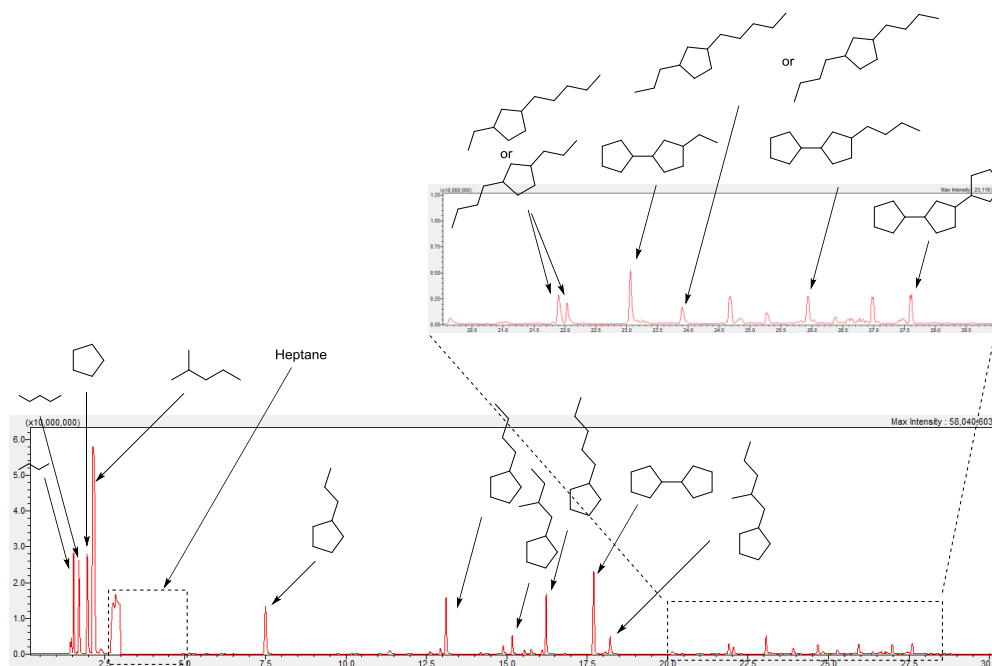


Figure 4.6 GC-MS chromatogram of the products obtained after hydrodeoxygenation of a product mixture obtained upon coupling of selected model alcohols with cyclopentanone. Reaction conditions: heptane solution 10 mL, Ni/Al₂O₃-SiO₂ 0.2 g, 250 °C, 6 h, H₂ 40 bar.

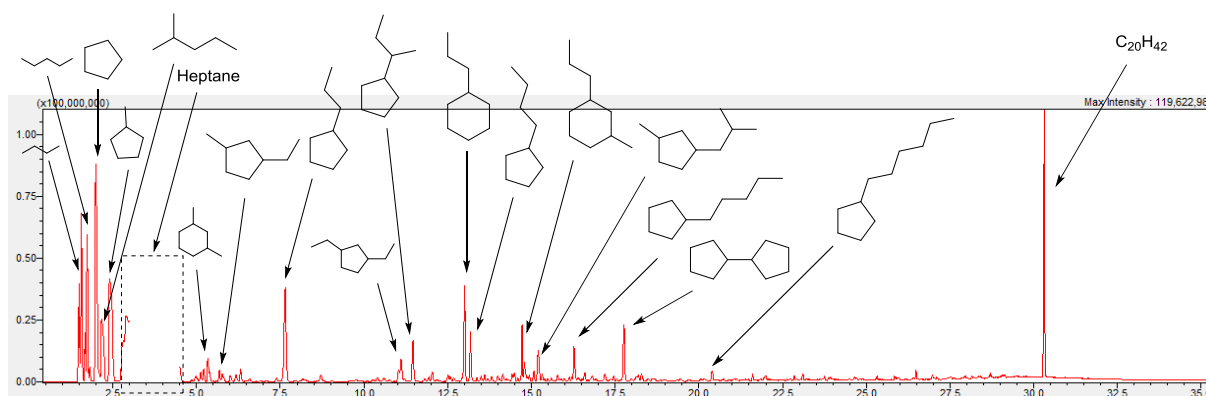


Figure 4.7 GC-MS chromatogram of the products obtained after hydrodeoxygenation of a product mixture obtained upon coupling of **SMix** (transferred to heptane) with cyclopentanone. Reaction conditions: heptane solution 10 mL, Ni/SiO₂-Al₂O₃ 0.2 g, 250 °C, H₂ 40 bar, 6 h, eicosane 20 mg.

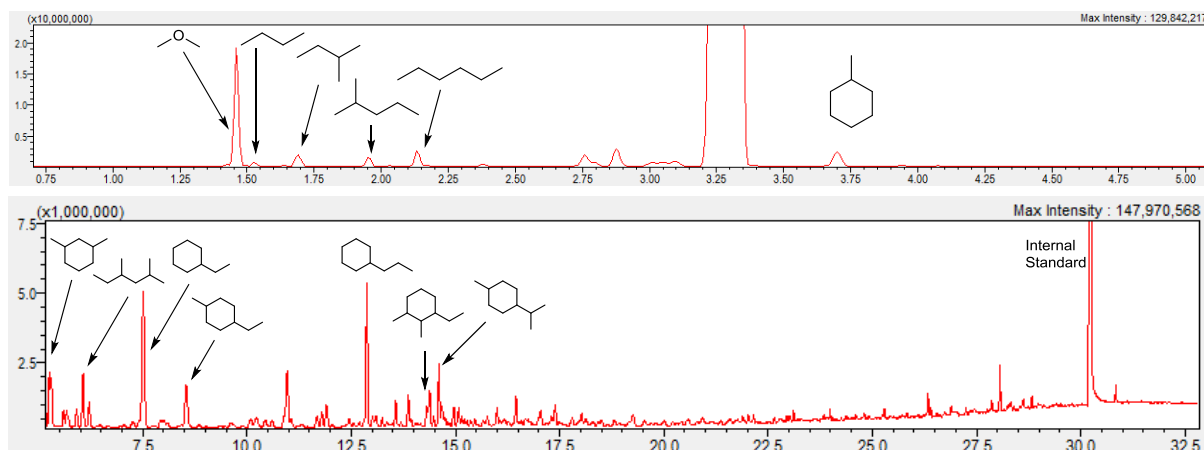


Figure 4.8 GC-MS chromatogram of the products obtained after hydrodeoxygenation when using the heptane insoluble oil. Reaction conditions: heptane solution 10 mL, Ni/SiO₂-Al₂O₃ 0.2 g, 250 °C, H₂ 40 bar, 6 h, eicosane 20 mg.

Since some components of the product mixture obtained after HDO were short chained, such as small amount of butane and other volatile alkanes detectable by GC-MS and GC-FID, the product quantification had to be carefully evaluated. Since the solubility of these short chain alkanes is highly dependent of the temperature³⁷ the workup of the reaction was repeated by cooling the reactor to 0 °C with ice water. When comparing Entry 1 to Entry 2 in Table 4.3 and also Figure 4.9, it can be seen that cooling the reactor substantially increased the yield of C₄ alkanes.

The products fell into two main categories: C₄–C₆ alkanes originating from branched or cyclic uncoupled alcohols, and transportation fuel range, C₈–C₁₁ alkanes which belong to the jet fuel range from the coupling of cyclopentanone with aliphatic alcohols in **SMix** and of lignin-derived propyl-cyclohexanols. The total amount of alkanes is 280.4 mg, which means 54% of the starting materials (cyclopentanone and **SMix**) are converted to this fuel range alkanes (For the calculation of carbon content and yield of alkanes, please see Chapter 4.4.4). Among all these alkanes, jet range (C₈-C₁₆) alkanes account for 31.6%. Although the yield of delivered alkanes especially jet range alkane is lower than most of the processes using platform chemicals (e. g. furfural and 2-methylfurfural), this process gives the first example of coupling complex alcohol mixture and the whole process is operated by using non-noble metal catalysts.

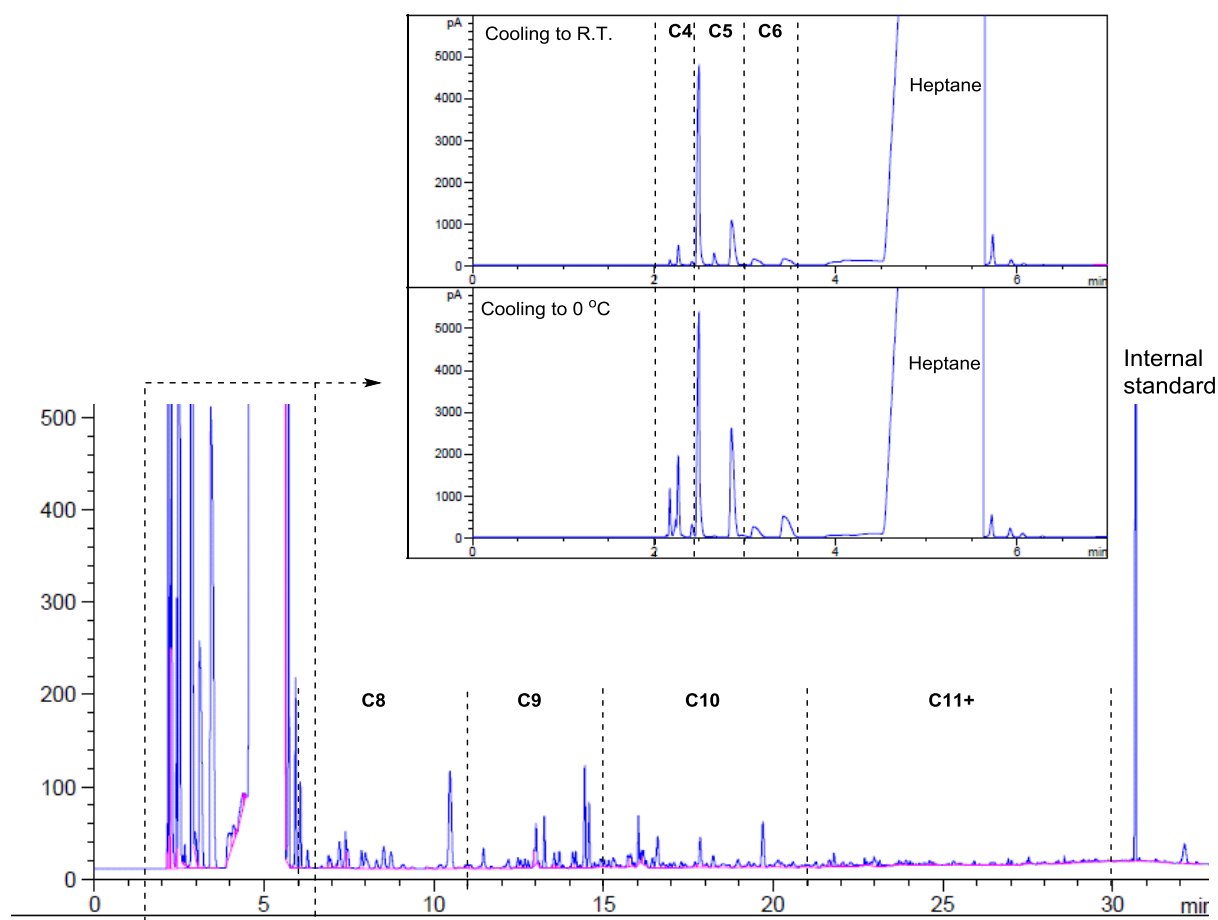


Figure 4.9 GC-FID chromatogram of the products obtained after hydrodeoxygenation when using a product mixture obtained upon coupling of **SMix** (transferred to heptane) with cyclopentanone. The inserted figure shows the comparison of the range of short alkanes when cooling to room temperature versus 0 °C after reaction. Reaction conditions: heptane solution 10 mL, Ni/SiO₂-Al₂O₃ 0.2 g, 250 °C, H₂ 40 bar, 6 h, eicosane 20 mg.

Table 4.3 Distribution of the products after HDO based on chain length.^a

Entry ^b	Weight (mg)							Total Alkanes	C8+ Alkanes
	C4	C5	C6	C8	C9	C10	C11+ ^c		
1	29.1	101.6	30.1	26.0	20.2	20.3	5.7	233.0	72.2
2	33.7	118.4	37.5	21.3	15.7	21.9	10.7	259.2	69.6
3	3.6	5.1	1.6	6.2	1.3	1.2	2.1	21.2	10.8
2+3	40.9	119.9	39.1	27.8	17.0	23.1	12.8	280.4	80.5
Entry ^b	Carbon content (mg) ^d							Total Alkanes	C8+ Alkanes
	C4	C5	C6	C8	C9	C10	C11+ ^c		
1	24.1	84.5	25.2	22.3	17.3	17.4	4.9	195.7	61.9
2	27.9	98.5	31.4	18.2	13.4	18.7	9.2	217.3	59.5
3	3.0	4.2	1.3	5.3	1.1	1.0	1.8	17.7	9.2
2+3	30.9	102.7	32.7	23.5	14.5	19.7	11.0	235.0	68.7

a. Due to the overlap with heptane, alkanes in the C₇ chain length range cannot be calculated, thus the current numbers are an underestimation of the actual carbon yield. b. Entry 1 shows the results using the heptane solubles and cooling to room temperature after HDO reaction, Entry 2 shows the results using heptane solubles and cooling to 0 °C by ice water after HDO reaction, Entry 3 shows the results using heptane insolubles and cooling to 0 °C by ice water after HDO reaction, c. Calculated as C₁₅. d. For the carbon content in

alkanes we use chemical formula C_nH_{2n+2} for C_4 , C_5 and C_6 as they are mainly linear or branched alkanes and C_nH_{2n} for C_{8+} as they are mainly cyclic alkanes. So the carbon content in entry 2 of C6 is 31.4 mg ($37.5 \times 83.6\%$) and C_{10} is 18.7 mg ($21.9 \times 85.6\%$).

4.3 Conclusions

In this Chapter, I have described the upgrading of **SMix** mixtures originating from the *LignoFlex* process to yield fuel range alkanes. The designed process includes a chain elongation step of coupling **SMix** with cyclopentanone using CuNi-PMO catalyst to get long chain ketones and a HDO process to produce alkanes using a commercial Ni catalyst. This two-step process finally deliver fuel range alkanes with a total yield of 54%. This process shows the possibility of coupling a complex alcohol mixture with cyclopentanone and the Ni/SiO₂-Al₂O₃ shows extremely high stability during recycling test.

However, in this process, not all alcohols are upgraded and leave a lot of short chain alcohols before HDO reaction. This means the CuNi-PMO catalyst is still not efficient enough; further research will focus on the development of more efficient coupling catalysts. On the other hand, the solvent change step will spend a lot of energy; a more efficient and low energy separation process would be really attractive. And it would be an ideal solution if a catalyst can do the coupling reaction in methanol is developed but how to avoid the participation of methanol in the coupling reaction would really difficult.

4.4 Experimental procedure

4.4.1 Coupling reactions of 1-pentanol with cyclopentanone

Coupling reactions of 1-pentanol with cyclopentanone were performed in a 10 mL Swagelok stainless steel microreactor. In a typical experiment, 1-pentanol and cyclopentanone were placed in the microreactor and heptane was added as solvent. Then specified amount of catalyst was added, the reactor was sealed and placed in a pre-heated aluminum block at the desired temperature. After the indicated reaction time, the microreactor was cooled down in an ice-water bath and the liquid sample was separated by filtration. The collected samples were then analyzed by GC-FID (Hewlett Packard 6890 series equipped with a HP-5 capillary column and a flame ionization detector) and GC-MS (Shimadzu GC-2010 plus system equipped with a GCMS QP2010 GC SE detector and a HP5 column). The following operating conditions were used: injection temperature of 300 °C, column temperature program: 40 °C (5 min), 10 °C /min to 280 °C (6 min), detection temperature of 300 °C.

4.4.2 Experimental procedure for solvent exchange and coupling

The methanol solution **SMix**, (generated from the catalytic processing of the lignocellulose residues in supercritical methanol, using 1 g pine lignocellulose as substrate) was separated from the catalyst by filtration, and was transferred to a 50 mL round bottom flask to which 10 mL heptane was added. Methanol was then removed by distillation in a special distillation

apparatus equipped with an oil/water separator filter funnel, at 105 °C. After distillation, a light yellow heptane solution containing most of the alcohol products was obtained. As can be seen from the GC-FID traces below, most of the aliphatic alcohols were successfully transferred into heptane, while there was also a small amount of heptane insolubles (~30 mg of brown oily material). The heptane solution (8 mL) was divided to two 4 mL portions and these were transferred to two identical 10 mL Swagelok stainless steel microreactors. Then cyclopentanone and CuNi-PMO catalyst were added. The reactors were sealed and placed in a pre-heated aluminum block at the desired temperature. After the indicated reaction time, the microreactors were cooled down in an ice-water bath and the liquid sample was separated by filtration with a PTFE filter (0.42 µm). The collected samples were then analyzed by GC-MS. To better understand the composition of the heptane insoluble oil, the sample was dissolved in 2ml DCM, since it is good polar solvent and cannot originate from the sample and the sample was analyzed by GC-MS.

4.4.3 Hydrodeoxygenation of the ketones obtained from the coupling of SMix with cyclopentanone to alkanes

Hydrodeoxygenation (HDO) reactions were carried out in a 100 mL high pressure Parr autoclave. In a typical experiment, the heptane solution containing 4-propylcyclohexanone or all the ketones after the coupling reaction was made up to 10 mL with additional heptane, and then transferred to the reactor. Ni/Al₂O₃-SiO₂ was added as catalyst and then the reactor was sealed and pressurized with 40 bar H₂. The reactor was heated to 250 °C and the stirring was kept at 400 rpm for 6h. After reaction the reactor was cooled to room temperature or 0 °C with ice water and the solution was analyzed in detail by GC-MS and GC-FID. The heptane insoluble part was dissolved in 0.4ml methanol while treated in an ultrasonication bath to help solubilization, then transferred to a 100 ml Parr reactor and 10ml heptane was added, the hydrodeoxygenation reaction was then carried out based on the same conditions above.

The recycling was performed as follows: After reaction the content of the reactor was transferred to a centrifuge tube with additional 4mL heptane and centrifuged. The heptane solution was separated from the catalyst by subsequent decantation. Fresh, 4 mL of heptane was added to the catalyst, ultrasonicated and centrifuged again. The heptane washings were combined and an additional 20 mg of eicosane was added as an internal standard. The leftover catalyst in the centrifuge tube and the glass insert were dried in a desiccator overnight at room temperature in vacuum. For the next run, the catalyst was transferred to the glass insert, its weight was determined, then 0.23 mL (1.5 mmol) of substrate and 10 mL of heptane were added and the filled glass insert was transferred to a 100 mL Parr® reactor and the catalytic procedure was performed. The whole procedure was repeated for 11 runs. Since the substrate was fully converted to propyl cyclohexane with 99% selectivity, double amount of substrate was used for 12th to 14th cycle and the substrate amount was gradually increased.

In order to minimize the loss of catalyst, the same centrifuge tube was used for the catalyst separation. After 20th cycles, only 81 mg catalyst was recovered and this means in average 6 mg catalyst was lost for each cycle during the recycling test.

For the recycling test, 4-propylcyclohexanone was selected as model compound. The catalyst showed extremely high robustness.

4.4.4 Determination of the yield of alkanes

In order to calculate the yield of alkanes obtained after hydrodeoxygenation, internal standard eicosane ($C_{20}H_{42}$) was added after reaction. Sensitivity factors of the products were obtained by ECN-based calculations due to lack of commercial standards.³⁸

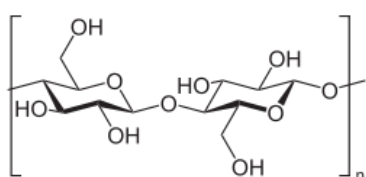
The weight of alkanes of different chain length (W_x) was calculated based on the equation:

$$W_x = \frac{C_{20} \cdot A_x \cdot W_{20} \cdot M_x}{C_x \cdot A_{20} \cdot M_{20}}$$

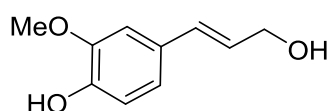
M_x : molar mass of the alkanes with certain chain length; C_x : carbon number of the alkanes with certain chain length; A_x : summary of peak areas of products have the same chain length. C_{20} : carbon number of internal standard; A_{20} : area of internal standard; W_{20} : weight of internal standard; M_{20} : molar mass of internal standard.

The carbon content of the solid residue and obtained alkanes was calculated as below

The weight of the solid residue was determined experimentally. From the analysis as described in Chapter 2.4.7, 1 g pine lignocellulose contains 286 mg lignin. We assumed that the solid residue (in total 790 mg) contains 714 mg carbohydrates, and the rest is unconverted lignin (76 mg). We further assumed that the chemical structure of the carbohydrates is described by that of cellulose (main component), a regular polymer consisting of glucose units.



The percentage of carbon in $(C_6H_{10}O_5)_n$ is therefore 44.4%. We used the basic phenol monomer coniferyl alcohol described by the chemical formula $(C_{10}H_{12}O_3)_n$ as main building block describing the unreacted lignin component.



The carbon percentage is therefore 66.7%. As a result the carbon content in solid residue is 368 mg ($714 \times 44.4\% + 76 \times 66.7\%$).

4.5 References

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